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(54) CATALYST FOR CATALYTIC REDUCTION OF NITROGEN OXIDE

(57)Abstract:

PURPOSE: To increase the purification efficiency of a ternary catalyst for simultaneous removal of NOx, hydrocarbon compds. and CO in exhaust gas within a wide range of fuel-air ratio by supporting a perovskite type multiple oxide represented by a specified formula on a solid acid carrier.

CONSTITUTION: A perovskite type multiple oxide represented by a formula $AxB1-xCyC1-yO3$ is supported on zeolite or other solid acid carrier to obtain a catalyst for simultaneous removal of NOx, hydrocarbon compds. and CO in exhaust gas. In the formula, A is La or Ce, B is Ba, Sr, Ca, Mg, Pb, Zn or Co, C is Fe, Ni, Cr, Cu, V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru or Pt, $0 \leq x \leq 1$ and $0 \leq y \leq 1$. When the catalyst is used, NOx and hydrocarbon in exhaust gas are efficiently removed within a wide range of fuel-air ratio.

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JAPANESE [JP,05-076762,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

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CLAIMS

[Claim(s)]

[Claim 1] The catalyst for removing to coincidence the nitrogen oxides, hydrocarbon compound, and carbon monoxide in the exhaust gas characterized by solid acid support coming to support the perovskite mold multiple oxide expressed with following the (1) type.

AXB1-XCYC1-YO3 (1)

(Among a formula, La, or Ce and B are [Mn, or Co and C of Ba, Sr, calcium, Mg Pb, Zn, or Ag and C] Fe, nickel, Cr, Cu, V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru, or Pt, and A is $0 \leq X \leq 1$ and $0 \leq Y \leq 1$.)

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application] This invention relates to the three way component catalyst used in case the harmful nitrogen oxides contained in the exhaust gas discharged from works, an automobile, etc., a hydrocarbon, and a carbon monoxide are removed to coincidence in detail with respect to the catalyst for nitrogen-oxides catalytic reduction.

[Description of the Prior Art] Since the reactions which remove injurious ingredients in exhaust gas, such as NOX, HC, and CO, to coincidence are the reaction which returns NOX to N2, and a reaction for which the reaction which oxidizes HC and CO in a carbon dioxide and water advances to coincidence and they become very important [the quantitative ratio of oxidizing quality components contained in exhaust gas, such as oxygen and NOX, and reducibility components such as HC and CO,], offgas treatment is performed on the conditions near theoretical air fuel ratio. However, operation by theoretical air fuel ratio became the cause of aggravation of fuel consumption, and development of a catalyst with a large window has been desired. Conventionally, as a three way component catalyst component, a platinum-rhodium-alloy, palladium-rhodium, and platinum-palladium-rhodium catalyst shows high activity, and the catalyst which supported the platinum rhodium alloy to the alumina is put in practical use. Moreover, since these precious metal catalysts are expensive, the catalyst which makes a perovskite mold multiple oxide or these contain palladium as a catalyst replaced with this has been proposed. however, any of these catalysts — although — only theoretical air fuel ratio or its neighborhood ratio showed high activity. (The width of face of a window is narrow) Therefore, development of the catalyst which has the window where width of face is wide has been desired, without sacrificing fuel consumption. This invention is made in view of the above situation, and the place made into the purpose is to offer the three way component catalyst which has the window where width of face is wide, and the three way component catalyst with which in other words the gap from theoretical air fuel ratio functions effectively on the bottom of a large exhaust gas condition.

[Means for Solving the Problem] Solid acid support, such as a zeolite, crystalline silicic acid aluminum phosphate (SAPO), crystalline aluminum phosphate (ALPO), crystalline phosphoric acid metal aluminum (MAPO), an alumina, a titania, a zirconia, and a silica alumina, comes to support the perovskite mold multiple oxide by which the catalyst for nitrogen-oxides catalytic reduction which uses the hydrocarbon and/or oxygenated compound concerning this invention as a reducing agent is expressed with following the (2) type.

AXB1-XCYC1-YO3 (2)

the inside of a formula, and A — La, or Ce and B — Ba, Sr, calcium, Mg, Pb, Zn, or Ag — C is Co, and Mn or C is Fe, nickel, Cr, Cu, V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru, or Pt, and it is $0 \leq X \leq 1$ and $0 \leq Y \leq 1$. The solid acid support in this invention means the support which shows solid acid nature in the temperature field used. The check of solid acid nature is in using the temperature programmed desorption which used ammonia, ammonia, or a pyridine. *situ* It is made by the FTIR method. As solid acid support, there are zeolite system solid acid support, oxide system solid acid support, etc. which are shown below.

(i) Zeolite system solid acid support processes the zeolite which is excellent in thermal resistance, such as Na-mordenite, Na-ZSM-5, and Na-USY (USY: ultra stay bull Y mold zeolite), from acids, such as a water solution of ammonium salt, such as an ammonium sulfate, or a sulfuric acid, and is obtained by carrying out the ion exchange of some or all of alkali metal in a zeolite to ammonium ion (NH_4^+) or a hydrogen ion (H^+). When based on the approach of carrying out the ion exchange by NH_4^+ , finally baking processing is needed. It is the acid type mordenite obtained by carrying out acid treatment of the mordenite mold zeolite expressed with following the (3) type, for example as zeolite system solid acid support. The acid type mordenite whose mole ratios of $\text{SiO}_2/\text{aluminum 2O}_3$ the mole ratios of $\text{SiO}_2/\text{aluminum 2O}_3$ are 13-20, and are 25-200, The zeolite obtained by carrying out the ion exchange of some or all of Ion M in the zeolite expressed with following the (4) type by Ti^{4+} , Zr^{4+} , or Sn^{4+} is mentioned.

M2 [(AlO_2)₂ r(SiO_2) 10] - ZH_2O (3)

(However, it is the value to which M is changed with alkali-metal ion among a formula, and r is changed according to the synthetic conditions of a zeolite.)

M'A [(AlO_2) p(SiO_2) q] - ZH_2O (4)

(However, ion M' is alkali-metal ion, alkaline-earth-metal ion or a hydrogen ion, $nA=p$ (n is the valence of Ion M), and $q/p \geq 5$ among a formula.)

(ii) — as oxide system solid acid support — aluminum2 — O3, TiO_2 , TiO_2/SO_4 , —, ZrO_2 , and ZrO_2/SO_4 — single metallic oxides, such as —, the multiple oxide of $\text{SiO}_2/\text{aluminum 2O}_3$, $\text{TiO}_2/\text{aluminum 2O}_3$, and $\text{TiO}_2/\text{ZrO}_2$ grade, etc. are mentioned. In these, aluminum 2O3 and SiO2 [ZrO_2 and]/aluminum 2O3 are desirable in respect of thermal resistance.

(iii) The crystalline aluminum phosphate (ALPO) of a kind which has the porous structure or the layer structure of zeolite resemblance as other examples of solid acid support, the crystalline phosphoric acid metal aluminum (MAPO) which permuted a part of crystalline silicic acid aluminum phosphate (SAPO) which is the close relationship matter, phosphorus of ALPO, or phosphorus-aluminum with metals, such as titanium, iron, magnesium, zinc, manganese, and cobalt, are mentioned. ALPO type phosphate can be adjusted to the combination of the request chosen from the above-mentioned phosphagen and the source of a metal, a silica and a silica sol, silicate of soda, etc. with a hydrothermal crystallization method under the case where a zeolite is compounded, and similar conditions, from the

aw material which mixed the so-called templates, such as an amine and quaternary ammonium. The main differences with the case where a zeolite is compounded are generally compounded more in pH acidity field by the elevated temperature (in general 150 degrees C or more). Generally the presentation of ALPO type phosphate is aluminum 2O3. -(0.8-1.2)- It is expressed with P2O5 and nH2O. Moreover, although the peaks of the silica which is permuted in SAPO or MAPO, and a metal are about about 1 of the total amount of aluminum and phosphorus / 10, they may use in this invention what is not necessarily contained in this presentation range, i.e., the thing containing an amorphous substance. When using as support the phosphate of the ALPO type obtained by the hydrothermal crystallization method, after rinsing and drying, generally what carried out incineration removal of the template which calcinates and remains in air is used. The catalyst concerning this invention can be adjusted by the approach of (1), (2), or (3) shown below. In the slurry which distributed solid acid support, (1) La, Ce, Ba, Sr, calcium, Mg, Pb, Zn, Ag, Mn, Co, Fe, nickel, Cr, Cu, By water-soluble salts, such as a nitrate of V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru, or Pt, the method of throwing an alcoholic solution into these alkoxides and making these neutralize or hydrolyze, etc. Solid acid support is made to support perovskite compound precursors, such as these compound metal kinds of hydroxide. Subsequently, it dries and calcinates, after repeating filtration, rinsing, and repulping and performing them.

(2) Fully carry out wet-grinding mixing of solid acid support and the perovskite compound adjusted separately by a planetary mill etc. (3) Precursors, such as a water-soluble salt of solid acid support, or a hydroxide, and La, Ce, Ba, Sr, calcium, Mg, Pb, Zn, Ag, Mn, Co, Fe, nickel, Settlings are made to generate by water-soluble salts, such as a nitrate of Cr, Cu, V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru, or Pt, the method of making the solution which mixed the alcoholic solution of these alkoxides to homogeneity neutralize or hydrolyze, etc. Subsequently, it dries and calcinates, after repeating filtration, rinsing, and repulping and performing these settling. In the above approach, the lower one of the generation temperature of a perovskite compound is desirable. The reason is that it is avoidable that the perovskite compound which has a big specific surface area is obtained, and the solid acid nature of solid acid support deteriorates by the reaction of solid acid support and the element which constitutes a perovskite compound, or the activity of a catalyst falls by the fall of the amount of generation of a perovskite compound, so that the generation temperature is low. therefore, aluminum2 — if it is when using solid acid support with high reactivity with the element which constitutes a perovskite compound like O3 and TiO2, the approach of of (3) which raises the homogeneity of the element which constitutes solid acid support, and the element which constitutes a perovskite compound is not desirable. Generally, although the approach of (1) is desirable, the catalyst which shows quite high activity also by the approach of (2) can be acquired. The suitable amount of support of a perovskite compound is 1.0 — 50 % of the weight to the AUW of this perovskite compound and solid acid support. If 50 % of the weight is exceeded, although the rate of purification of a hydrocarbon or a carbon monoxide by oxygen becomes high in the system of reaction with which the addition effectiveness according to increase in quantity is not not only acquired, but oxygen coexists, the rate of purification of NOX will fall greatly. On the other hand, at less than 1.0 % of the weight, NO, a hydrocarbon, and any rate of purification of CO cannot be raised enough. The catalyst concerning this invention can be conventionally fabricated in the shape of a honeycomb, and the various configurations of spherical ** by the well-known shaping approach. In the case of this shaping, a shaping assistant, a Plastic solid reinforcement object, an inorganic fiber, an organic binder, etc. may be blended suitably. Moreover, covering support can be carried out by the wash coat method etc. on the base material fabricated beforehand. In addition, it can also be conventionally based on the well-known catalyst preparation. Although the optimal temperature the catalyst concerning this invention indicates purification activity to be to nitrogen oxides, a hydrocarbon, and a carbon monoxide changes with catalyst kinds, it is usually 100—800 degrees C, and it is desirable in this temperature field to carry out conduction of the exhaust gas about (space—velocity SV) 500—100,000. In addition, a more suitable service temperature field is 200—800 degrees C. moreover, the air—fuel ratio (A/F) as which the catalyst concerning this invention functions effectively — 14.0—60 — it is — desirable — 14.0—40 — it is 14.0—30 more preferably.

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

(1) Respectively, 101.05g, 135.83g weighing capacity of adjustment example 1La(NO3)2.6H2O of a catalyst, Mn(Ac)2.4H2O (the same is said of Ac:CH3COOH and the following), Sr (NO3)2, and the Co(NO3)2.6H2O was carried out, and they were melted in 500ml water 74.08g 28.60g. The NaOH water solution of 121 g/l was added to this solution, fully stirring, and pH was set to 10. It riped by continuing stirring for 18 hours after neutralization termination. then, filtration, rinsing, and repulping — the conductivity of filtered water — repulping — it repeated until it became almost the same as service water. The obtained filter cake was dried at 120 degrees C for 18 hours, and, subsequently it calcinated at 700 degrees C for 3 hours. As a result of calculating XRD of the obtained baking object, it turned out that the perovskite crystal phase is generating. Moreover, the specific surface area (the following specific surface area is also depended on the law) by the BET adsorption method of this baking object was 23.7m2/g (La0.4Sr0.6Co0.8Mn 0.2O3). Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of activity titanium oxide which calcinates the metatitanic acid (TiO2andH2O) obtained according to the sulfuric-acid method titanium oxide process for 3 hours, and obtained it at 600 degrees C] (specific surface area: 104.2m2/g) mixture, in the planetary mill, grinding mixing was carried out for 30 minutes, viscosity control was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-1) was obtained. The coverage of the slurry at this time was 0.116g per honeycomb 1cc.

50.66g weighing capacity of example 2La(NO3)2.6H2O and the 89.5g Mn(Ac)2.4H2O was carried out respectively, and, subsequently the perovskite compound (LaMnO3) was obtained by the same approach as Example I. The specific surface area of this perovskite compound was 29.1m2/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-2) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.094g per honeycomb 1cc.

50.66g weighing capacity of example 3La(NO3)2.6H2O, Pb (NO3)2, and the 71.60g Mn(Ac)2.4H2O [13.69g] was carried out respectively, it mixed, and, subsequently the perovskite compound (La0.8Pb0.2MnO3) was obtained by the same approach as Example I except having calcinated at 800 degrees C for 3 hours. The specific surface area of this perovskite compound was 23.7m2/g. Thus, in

addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-3) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.117g per honeycomb 1cc.

59.19g weighing capacity of example 4La(NO₃)₂·6H₂O and the 88.07g Co(NO₃)₂·6H₂O was carried out respectively, it mixed, and, subsequently the perovskite compound (LaCoO₃) was obtained by the same approach as Example 1 except having calcinated at 800 degrees C at 3:00. The specific surface area of this perovskite compound was 17.47m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and H form mordenite (HM-23) 100g [by the Japanization study company] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-4) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.113g per honeycomb 1cc.

59.19g weighing capacity of example 5Ce(NO₃)₂·6H₂O, Ba (NO₃)₂, and the 70.65g Co(NO₃)₂·6H₂O [10.63g] was carried out respectively, and, subsequently the perovskite compound (Co_{0.8}Ba_{0.2}CoO₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 23.0m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and H form mordenite (trade name "HM-23") 100g [by the Japanization study company] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-5) of 1.25mm pitch honeycomb configuration was obtained. The coverage of the slurry at this time was 0.130g per honeycomb 1cc.

339.0ml weighing capacity of example 6La(NO₃)₂·6H₂O, Mn(Ac)₂·4H₂O, and the 90.84g (water solution of 14.82g/100ml concentration as Ti) of the 25.71g of the TiCl₄ water solutions was carried out respectively, and, subsequently the perovskite compound (LaMn_{0.5}Ti_{0.5}O₃) was obtained by the same approach as Example 1. The specific surface area of this perovskite compound was 25.3m²/g. Thus, in addition to [100g of water] 10g of obtained perovskite compounds, and silica-alumina (trade name "COK-84") 100g [made from Japanese AROJIRU] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-6) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.098g per honeycomb 1cc.

The ethanol solution of La ethoxide by example 7 <preparation of perovskite compound> Hakusui Chemical Industries (solution of 73 g/l concentration as La₂O₃), 9.22ml weighing capacity is carried out and it mixes, and stirring enough, 1% of the weight of the aqueous ammonia solution was dropped gradually, and the ethanol solution (solution of 79 g/l concentration as BaO) of company Ba ethoxide, the ethanol solution (solution of 67 g/l concentration as NiO) of company nickel ethoxide, and 49.95ml (solution of 91g [/l.] concentration as CoO) of 21.74ml of 100.0ml of ethanol solutions of Co ethoxide were made to hydrolyze respectively. Subsequently, evaporation to dryness was carried out, carrying out homogeneity mixing of this, it calcinated at 600 degrees C for 3 hours, and the perovskite compound (La_{0.8}Ba_{0.2}Co_{0.8}Nickel_{0.2}O₃) was obtained. The specific surface area of this perovskite compound was 36.9m²/g.

Aluminum isopropoxide 90.7g broken finely was added to 129.6g of <preparation of SAPO-34> water small quantity every, stirring, and stirring mixing was carried out until it became homogeneity. 51.3g of phosphoric acid water solutions was dropped at this mixed liquor 85%, and after carrying out stirring mixing until it became homogeneity, stirring mixing was fully carried out [silica sol 16.0g] 50 more%. Subsequently, hydroxylation tetraethylammonium 81.6g was added and stirring mixing was fully carried out. After having carried out filtration separation of the product after it taught this mixture to the autoclave and it carried out the stirring reaction at 200 degrees C for 24 hours, and rinsing and drying further, it calcinated in 3-hour air at 500 degrees C, and SAPO-34 were obtained. These SAPO-34 were the thing of 9.5 and the presentation contained 18.0 or 19.0% of the weight about Si, aluminum, and P, respectively. Thus, 100g of water was added to the mixture of perovskite compounds [which were obtained / 25g and 100g] SAPO-34, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-7) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.138g per honeycomb 1cc. Weighing capacity of 101.05g, 74.08g, 135.83g, and the 33.60g was carried out respectively, example 8La(NO₃)₃·6H₂O, Sr (NO₃)₂, Co (NO₃)₂·6H₂O, and Fe(NO₃)₂·6H₂O were mixed, and the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 21.6m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-8) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.098g per honeycomb 1cc.

Weighing capacity of 202.10g, 28.41g, 135.83g, and the 28.19g was carried out respectively, example 9La(NO₃)₃·6H₂O, Zn(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, and Cu(NO₃)₂ and 3H₂O were mixed, and the perovskite compound (La_{0.8}Zn_{0.2}Co_{0.8}Cu_{0.2}O₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 17.3m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-9) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.083g per honeycomb 1cc.

Weighing capacity of 202.10g, 19.82g, 135.83g, and the 69.87g was carried out respectively, example 10La(NO₃)₃·6H₂O, AgNO₃, Co (NO₃)₂·6H₂O, and Zr(NO₃)₄ and 5H₂O were mixed, and the perovskite compound (La_{0.8}Ag_{0.2}Co_{0.8}Zr_{0.2}O₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 17.3m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-10) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.097g per honeycomb 1cc.

example 11La(NO₃)₃·6H₂O — O, Sr (NO₃)₂, and Co(NO₃)₂·6H₂O — weighing capacity of each 101.05g, 74.08g, 135.83g, and 27.79g was

carried out, O and Cr (NO₃)₃ were mixed, and the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.8}Cr 0.2O₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 20.3m²/g.

45.8g (what contains 9.5% of acetic acids alumina 67%) of pseudo-boehmite powder was added to 69.2g of phosphoric acid, and 178g [of water] mixture small quantity every <preparation of ALPO-5> 85%, and stirring mixing was carried out until it became homogeneity. Tripropylamine 43.8g was added to this liquid, and stirring mixing was carried out until it became homogeneity. After teaching this mixture to the autoclave and carrying out a stirring reaction at 150 degrees C for 70 hours, filtration separation of the product was carried out, after rinsing and drying, it calcinated in 3-hour air at 500 degrees C, and ALPO-5 were obtained. These ALPO-5 were the thing of the presentation which contains aluminum and P 18.0 or 22.0% of the weight, respectively. Thus, in addition to [100g of water] the mixture of perovskite compounds [which were obtained / 30g and 100g] ALPO-5, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-11) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.104g per honeycomb 1cc.

216.81ml weighing capacity of the 74.08g 101.05g [135.83g] was carried out respectively, it mixed, example 12 <preparation of perovskite compound> La(NO₃)₂·2H₂O, Sr (NO₃)₂, Co(NO₃)₂·2H₂O, and NbCl₅ (a hydrochloric-acid water solution, solution of 50 g/l concentration as Nb) were made into the example 1 below, and the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.8}Nb 0.2O₃) was obtained. The specific surface area of this perovskite compound was 18.9m²/g.

Stirring mixing was carried out until it added aluminum iso prop KISHIDO 56.3g broken finely small quantity every and became homogeneity, stirring first manganese of <preparation of MAPO-5> acetic acid 4.9g, and 4.1g of cupric acetate in the liquid which dissolved in 129g of water. Stirring mixing was carried out until it became homogeneity in this liquid [small quantity every], stirring 55.4g [of phosphoric acid], and diethyl ethanolamine 56.3g, and the mixed liquor of 55.5g of water 85%. After teaching this liquid to the autoclave and making it react at 200 degrees C for 25 hours, filtration separation of the product was carried out, after rinsing and drying, it calcinated in 3-hour air at 500 degrees C, and MAPO-5 were obtained. These MAPO-5 were the thing of 19.0, 19.0, and the presentation contained 2.8 or 4.4% of the weight about aluminum, P, Mn, and Cu, respectively. Thus, in addition to [100g of water] the mixture of perovskite compounds [which were obtained / 25g and 100g] MAPO-5, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-12) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.116g per honeycomb 1cc.

In example 13 example 1, it replaced with activity titanium oxide and the prototype sample (A-13) was obtained like the example 1 except having used ZrO₂ (specific surface area: 148.3m²/g) which calcinated zirconium hydroxide for 3 hours and obtained it at 600 degrees C. The coverage of the slurry at this time was 0.139g per honeycomb 1cc.

Respectively, 88.07g, 50.66g weighing capacity of example 14 <preparation of perovskite compound> La(NO₃)₂·2H₂O, Sr (NO₃)₂, and the Co(Ac)₂·2H₂O was carried out, and they were melted in 500ml water 10.76g. It was dropped fully stirring the NaOH water solution of 121 g/l, and pH of liquid was set to 10. It riped by continuing stirring for 18 hours after neutralization termination. then, filtration, rinsing, and RIPARUBU — the conductivity of filtered water — RIPARUBU — after repeating until it became almost the same as it of service water, the filter cake was dried at 120 degrees C for 18 hours. this dry matter was ground, 25.90ml (water solution of 100 g/l concentration as V) of oxalic acid vanadyl solutions was added to this grinding object, and it kneaded enough — evaporation to dryness was carried out, and it dried at 120 degrees C for 18 hours, subsequently it calcinated at 850 degrees C for 3 hours, and the perovskite compound (La_{0.8}Sr_{0.2}Co_{0.8}V_{0.2}O₃) was obtained. The specific surface area of this perovskite compound was 12.8m²/g. It mixed enough, having carried out 97.20g weighing capacity of the 100.0g of the silica sol O molds (thing of 20-% of the weight concentration as SiO₂) and zirconium chlorides (ZrCl₄) by the preparation > Nissan chemistry company of a <silica-zirconia, and stirring them respectively, and the total amount was set to 500ml with water. The NaOH water solution of 121 g/l was dropped at this liquid, and pH was set to 10. Stirring was continued after neutralization termination for 18 hours, filtration, rinsing, and RIPARUBU were repeated after that, the filter cake was obtained, at 120 degrees C, it dried for 18 hours and this filter cake was calcinated for 3 hours. The specific surface area of the obtained baking object was 297m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of the above-mentioned baking objects] mixture, ***** mixing during 30 minutes was carried out in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-14) was obtained. The coverage of the slurry at this time was 0.127g per honeycomb 1cc.

In the example 15 <preparation of perovskite compound> example 14, the perovskite compound (La_{0.8}Sr_{0.2}Co_{0.8}Mo 0.2O₃) was obtained like the example 14 except having replaced with the oxalic acid vanadyl water solution, and having added 260.22ml (water solution of 25 g/l concentration as MoO₂) of ammonia nature water solutions of an ammonium molybdate.

It held at 70 degrees C for 1 hour, having been immersed in the zirconium nitrate water solution (referred to as ZrO₂ thing of 100 g/l concentration), and stirring Na mordenite (NM-100P) 100g by the <preparation of Zr-mordenite> Japanization study company, and the ion exchange of Na was carried out to Zr. It calcinated at 650 degrees C after drying the zeolite cake rinsed [was filtered and] and obtained for 4 hours. The content of Zr of this zeolite (Zr-mordenite) was 3.3 % of the weight, and specific surface area was 391m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and Zr-mordenite 100g mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-15) was obtained. The coverage of the slurry at this time was 0.135g per honeycomb 1cc.

In example 16 example 14, the perovskite compound (La_{0.8}Sr_{0.2}Co_{0.8}Mo_{0.2}O₃) was obtained like the example 14 except having replaced with the oxalic acid vanadyl water solution, and having added 23.58g (50% of the weight of water solution as WO₃) of ammonium metatungstate water solutions. The specific surface area of this perovskite compound was 13.6m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, ***** mixing was carried out in the planetary mill for 30 minutes, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-16) was obtained. The coverage of the slurry at this time was 0.135g per honeycomb

cc.

respectively, weighing capacity of 173.20g, 126.98g, 276.48g, and the 25.90g was carried out, and example 17 La(NO₃)₃·6H₂O, Sr (NO₃)₂·6H₂O, and H₂PtCl₆·6H₂O were melted in 1000ml water. While 121 g/l carried out NaOH water-solution stirring, it was dropped at this water, and pH was set to 10. Stirring was continued after hydrolysis reaction termination for 18 hours. The perovskite compound (La_{0.4}Sr_{0.6}Co_{0.95}Pt 0.05O₃) was obtained like the example 1 below. The specific surface area of this perovskite compound was 27.6m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-17) was obtained. The coverage of the slurry at this time was 0.123g per honeycomb 1cc.

In example 18 example 17, it replaced with H₂PtCl₆·6H₂O, and Rh(NO₃)₃·3H₂O was made into the same approach as an example 17 except having used 16.25g, and the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.95}Rh 0.05O₃) was obtained. The specific surface area of this perovskite compound was 29.6m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-18) was obtained. The coverage of the slurry at this time was 0.129g per honeycomb 1cc.

In example 19 example 17, the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.95}Pd 0.05O₃) was obtained like the example 17 except having replaced with H₂PtCl₆·6H₂O, and having used 8.67g for PdCl₂. The specific surface area of this perovskite compound was 28.5m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-19) was obtained. The coverage of the slurry at this time was 0.122g per honeycomb 1cc.

In example 20 example 17, the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.95}Ru 0.05O₃) was obtained like the example 17 except having replaced with H₂PtCl₆·6H₂O, and having used 16.15g for RuCl₄ and 5H₂O. The specific surface area of this perovskite compound was 25.3m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-20) was obtained. The coverage of the slurry at this time was 0.129g per honeycomb 1cc.

In example 21 example 3, the prototype sample (A-21) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except ** which used a perovskite compound (LaCoO₃) and 1g (trade name "HM-23") of 100g of H mold mordenites by the Japanization study company respectively. The coverage of the slurry at this time was 0.929g per honeycomb 1cc.

In example 22 example 3, the prototype sample (A-21) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except having used a perovskite compound (LaCoO₃) and 10g (trade name "HM-23") of 100g of H mold mordenites by the Japanization study company respectively. The coverage of the slurry at this time was 0.948g per honeycomb 1cc.

In example 23 example 3, the prototype sample (A-23) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except having used a perovskite compound (LaCoO₃) and 50g (trade name "HM-23") of 100g of H mold mordenites by the Japanization study company respectively. The coverage of the slurry at this time was 0.109g per honeycomb 1cc.

In example 24 example 3, the prototype sample (A-24) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except having used a perovskite compound (LaCoO₃) and 50g (trade name "HM-23") of 100g of H mold mordenites by the Japanization study company respectively. The coverage of the slurry at this time was 0.122g per honeycomb 1cc.

Example 25 empirical formula: It was immersed into 1l. of 0.025 mols [/l.] TiOSO₄ water solutions, and 100g (made in Japanese Mobile, a trade name "ZSM-5", Y/X -35) of commercial items of the sodium mold mordenite expressed with Na_x[AlO₂] X and (SiO₂) Y, and ZH₂O was fully stirred. After having carried out the temperature up with the programming rate of 100 degrees C/o'clock, having held at 125 degrees C for 1 hour, making TiOSO₄ hydrolyze and carrying out the ion exchange of Na by Ti, stirring this in an autoclave, the ** exception, it rinsed and the cake of a zeolite was obtained. Subsequently, after drying this cake, it calcinated at 650 degrees C for 4 hours, and the zeolite was obtained. The content of Ti in this zeolite was 2.4 % of the weight as TiO₂. Thus, the prototype sample (A-25) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except having replaced with and used obtained Ti-ZSM -5 for H mold mordenite. The coverage of the slurry at this time was 0.110g per honeycomb 1cc.

In example of comparison 1 example 1, activity titanium oxide was not used, but the slurry for wash coats was obtained only using the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.8}Mn 0.2O₃), and others obtained the comparison sample (B-1) of the honeycomb configuration of 1.25mm pitch like the example 1. The coverage of the slurry at this time was 0.132g per honeycomb 1cc.

(2) The purification trial of nitrogen oxides CO and C₃H₆ content gas was performed by A/F changing the range of 14.0-40 to the evaluation test above-mentioned sample (A-1) - (A-25) a list by the following test condition about a comparison sample (B-1).

(Test condition)

(1) Gas presentation NO 1000ppmCO 1%C3H₆ 1000ppmCO₂ 10%A/F 14-40 (2) space velocity 10000 l/Hr (3) reaction temperature 300 degrees C, 400 degrees C, 500 degrees C, or 600-degree-C result is shown in Table 1 - 3.

表 1

反応温度300℃

	A/F								
	14.6			20.0			40.0		
	NO	HC	CO	NO	HC	CO	NO	HC	CO
A-1	72	99	93	89	99	99	77	99	99
A-2	65	98	90	84	99	99	73	99	99
A-3	59	95	88	83	99	95	76	99	97
A-4	74	99	93	92	99	99	81	99	99
A-5	69	97	87	84	98	99	73	99	99
A-6	65	98	89	85	99	99	75	99	99
A-7	84	99	99	95	99	99	87	99	99
A-8	74	97	96	86	99	99	76	99	99
A-9	71	95	90	86	98	93	78	99	98
A-10	79	99	93	73	99	99	65	99	99
A-11	68	98	95	81	99	98	72	99	99
A-12	65	98	92	84	99	99	75	99	99
A-13	70	99	95	92	99	99	81	99	99

	14.6			20.0			40.0		
	NO	HC	CO	NO	HC	CO	NO	HC	CO
A-14	62	97	88	80	97	91	73	98	95
A-15	55	93	81	79	95	90	73	97	95
A-16	58	95	84	79	97	93	75	98	95
A-17	78	99	99	85	99	99	79	99	99
A-18	74	99	99	81	99	99	70	99	99
A-19	75	99	99	82	99	99	73	99	99
A-20	79	99	99	87	99	99	81	99	99
A-21	49	63	55	56	71	62	45	74	68
A-22	75	98	92	70	99	98	61	99	99
A-23	79	99	93	73	99	99	65	99	99
A-24	82	99	99	65	99	99	58	99	99
A-25	61	97	90	85	99	98	78	99	99
B-1	70	99	92	4	99	99	0	99	99

表 2

A/F = 2.0における温度特性

図表 A-4

			400°C			500°C			600°C		
			NO	HC	CO	NO	HC	CO	NO	HC	CO
300°C	92	99	99	90	99	99	75	99	99	48	99

From Table 1 - 2, the catalyst [prototype sample (A-1) concerning this invention - (A-25)] all understand that the rate of purification is low generally to a thing with high nitrogen oxides, CO, and rate of purification of C3H6 for a comparison catalyst [comparison sample (B-1) and (B-2)].

[Effect of the Invention] As explained to the detail above, this invention does the outstanding characteristic effectiveness so — the three way component catalyst concerning this invention can purify efficiently the nitrogen oxides CO and the hydrocarbon in exhaust gas in the range of large A/F.

[Translation done.]